Solvent free selective oxidation of benzyl alcohol to benzaldehyde using a membrane contactor unit

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Abstract

A new clean catalytic process for the selective oxidation of benzyl alcohol with hydrogen peroxide to benzaldehyde has been studied. Neither solvent nor promoters are needed: a polymeric microporous membrane acts as a barrier to "keep in contact" the two phases: the organic phase, containing the substrate and the product, and the aqueous phase with the oxidant. Being the two phases separated by the membrane, there is no mix of them and dispersion phenomena do not occur. The species are transferred from one phase to the other only by diffusion.

The effect of various reaction parameters such as reaction temperature, type of membrane, type of catalyst, the addition mode of hydrogen peroxide was investigated.

Three different membranes based on hydrophobic polyvinilidene fluoride (PVDF) were prepared by phase inversion technique induced by nonsolvent and used as membrane contactor. The membranes are characterized by different thicknesses, porosity, tortuosity and hydrophobicity. The catalysts used were ammonium molybdate, $(NH_4)_6Mo_7O_{24}$ and sodium tungstate, Na_2WO_4. In literature, both these catalysts were reported to be effective in the oxidation of alcohols with H_2O_2 in combination with a phase transfer catalyst in chlorinated solvents.

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Keywords: Selective oxidation; Solvent free reaction; Hydrogen peroxide; Membrane contactor; Sustainable process

1. Introduction

There is a growing need for "green" technologies in the synthesis of fine chemicals and pharmaceuticals intermediates. In this context, an important target is to achieve the highest possible selectivity and thus minimize the additional costs of separation of by-products and waste removal that may be a critical factor in a small scale synthesis [1].

Oxidation of alcohols to aldehydes, in particular benzyl alcohol (BzOH) to benzaldehyde (BzH), is an important organic transformation. BzH is a very valuable chemical which has widespread applications in perfumery, dyestuff and agro chemical industries [2–4].

Conventional methods for performing such transformations generally involve the use of stoichiometric or more than stoichiometric quantities of inorganic oxidants, such as

chromium (VI) reagents, dimethyl sulfoxide, permanganates, periodates or *N*-chlorosuccinimide (NCS) [4].

The increasing demand for environment-conscious chemical processes has impelled many researchers to explore truly efficient oxidation methods using aqueous H_2O_2, an ideal oxidant in this context: hydrogen peroxide is by far the least environmentally demanding among the peroxides; in fact, water is the only by-product of these reactions. However, hydrogen peroxide is a rather weak oxidant. Thus in order to become synthetically significant, the oxidations by hydrogen peroxide need to be catalyzed [5]. Among the oldest, but very efficient, catalysts which have been well studied [6–9], the derivatives of some transition metal ions, i.e. V, Mo and W, in their highest oxidation states, are still under active investigation. The metal precursor adds hydrogen peroxide in an equilibrium process largely shifted to the right [10]. The intermediate **1** is thus formed in which *n* is usually 1 or 2 (Scheme 1).

The peroxometal complex **1** is the real oxidant in solution. Species such as **1** can be, in several instances, isolated and

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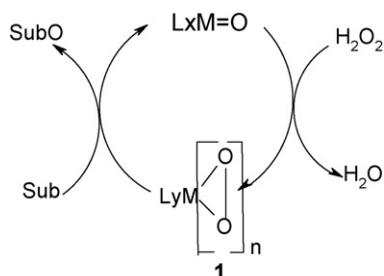
Scheme 1. Mechanism of peroxometal catalysis.

stored: they may be used as stoichiometric oxidants with synthetic relevance [11,12].

Anionic peroxomolybdenium complexes, for example, rendered soluble in chlorinated solvents by the presence of a lipophilic counter cation, allowed to obtain in a monophasic system quantitative yields of aldehydes from primary alcohols [11].

An alternative procedure consisted in a two-phase method oxidation with hydrogen peroxide under phase transfer conditions: a neutral lipophilic ligand acts as extracting agent. For example, the commercial ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in combination with a phase transfer catalyst, $(n\text{-}C_4H_9)_4NCl$, and a base (K_2CO_3), catalyzed the selective oxidation of secondary alcohols with H_2O_2 in THF solvent with a molar ratio alcohol:H_2O_2:catalyst of 10:40:1. The more hindered alcohol moiety was selectively oxidized in the presence of a less hindered one with a conversion of 90% in 6 days [13]. $Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$ were used as catalysts and a lipophilic tetraalkylammonium compound as extracting agent in the oxidation of primary and secondary alcohols in 1,2-dichloroethane by Bortolini et al. [14]. The molar ratio alcohol:H_2O_2:catalyst was of 10:20.2:1.

For all the peroxo complexes generated *in situ* by using commercial Mo(IV), W(IV), an excess of H_2O_2 was used. In fact, a problem of aqueous hydrogen peroxide as oxidant rises from its poor stability because it is liable to decompose while heated or in the presence of many metal ions. Therefore, there is a competition between the decomposition reaction and oxidation reaction. To overcome this problem, the peroxo anions of Mo(VI), W(VI) metals carrying active oxygen atoms should easily enter the organic phase. From this point of view, phase transfer agent must be able to extract the peroxo anions into organic phase. Shi and Wei [15] synthesized bis-quaternary phosphonium salts of peroxotungstate and peroxomolybdate in which the cation and counteranion are all bivalent: owing to the effective association between the two opposite charge, the peroxo anion carrying active oxygen atoms enters organic phase effectively.

In this work, we report a novel method for selective oxidation of BzOH to BzH. Neither solvent nor promoters are needed: a polymeric microporous membrane acts as a barrier to ''keep in contact'' the organic phase containing the BzOH and the BzH and the aqueous phase with hydrogen peroxide. The

species are transferred from one phase to the other only by diffusion: the membrane's role in the system studied in this work was to improve the contact between the two different reactive phases, the catalyst being physically separated from the membrane, realizing an inert membrane reactor [16,17]. The reaction between the reactants, controlled by diffusion across membrane, overcomes the limit of side reactions as over oxidation of the BzH to benzoic acid (BzA).

The chemical and engineering community is already paying significant attention to the request for technologies that would lead the goal of technological sustainability [18,19]. A promising example with a lot of interest by process engineers is the strategy of process intensification. It consists of innovative equipment, design and process development methods that are expected to bring substantial improvements in chemical and any other manufacturing and processing such as decreasing production costs, equipment size, energy consumption, waste generation. Membrane operations, with their intrinsic characteristics of efficiency and operational simplicity, high selectivity and permeability for the transport of specific components, low energetic requirement, good stability under operating conditions and environment compatibility, easy control and scale-up, represent an interesting answer for the rationalization of chemical production. Among new unit operations involving membranes, membrane contactors are expected to play a decisive role in this scenario. The key concept is to use a solid, porous, hydrophobic (or hydrophilic) polymer matrix in order to create an interface for mass transfer and/or reaction between two phases. Whereas the design of the conventional devices is restricted by limitations in the relative flows of the fluid streams, membrane contactors give an active area, which is independent of the liquid fluid dynamics [20].

In the oxidation of BzOH to BzH using a membrane contactor unit, described in this work, various reaction parameters such as reaction temperature, type of membrane, type of catalyst, the addition mode of hydrogen peroxide were investigated. Being a pioneering study, a reaction time of 4 h without analyzing the system lifetime in long time runs was investigated.

Three different membranes based on hydrophobic poly-vinilidene fluoride (PVDF) were prepared by phase inversion technique induced by nonsolvent [21] and used as membrane contactor. The membranes are characterized by different thicknesses (30 µm, 50 µm and 70 µm), porosity, tortuosity and microstructures (finger or nodular like).

The catalysts used were commercial sodium tungstate, Na_2WO_4 and ammonium molybdate, $(NH_4)_6Mo_7O_{24}$. From both an economic and environmental viewpoints, the selective system proposed in this study working in absence of organic solvents has as consequence the reduction of toxic waste and by-products making the process ecologically more acceptable. In fact, one of the major problems encountered in various processes for producing organic fine chemicals, is the use of organic solvents. Hence, it is appropriate that organic transformations under solvent-free conditions are attracting increasing attention [22].

2. Theory

2.1. Mass transport model

Due to the ''compartimentalization'' of the two reagents reactions, the mass-transfer processes involved in bringing the reactants together and product oxygenates diffusing out off the membrane may have a strong influence over the complete catalytic performance (Scheme 2).

For an optimal performance, resistances to mass transport should be minimized and reaction should be carried out in a reaction-limited regime.

All the membranes used in this work are asymmetric porous (see Section 3, Table 1). Therefore, the diffusivity through them (D_{eff}) differs from diffusivity on the bulk (D_0). The value of D_{eff} is in general determined by porosity (ε), tortuosity (τ) of the porous structure and from steric hindrance:

$$D_{eff} = \frac{D_0 \varepsilon}{\tau \Theta} \tag{1}$$

with

$$\Theta = [1 - r_s/r_p]^4 \tag{2}$$

where r_s is the Stokes radius of the reagent and r_p the mean radius of the pore [23].

3. Experimental

3.1. Chemicals

BzOH (MW = 108.14 g/mol, purity 99.99%) from Sigma-Aldrich was used both as reagent and as solvent. BzH (MW = 106.12 g/mol, purity 99.99%) and BzA (MW = 122.12 g/mol, purity 99.99%) from Sigma-Aldrich were used for analytical calibrations. Ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (MW = 1235.86 g/mol, purity 99.98%), sodium tungstate dihydrate, $Na_2WO_4\cdot2H_2O$ (MW = 329.85 g/mol, purity 99.99%) from Sigma-Aldrich were employed as catalysts. Hydrogen peroxide H_2O_2 (30 wt% solution in water) from Sigma-Aldrich was the oxidant.

For the preparation of polymeric membranes, PVDF Solef 6020 was supplied from Solvay Inc.; *N,N*-dimethylacetammide
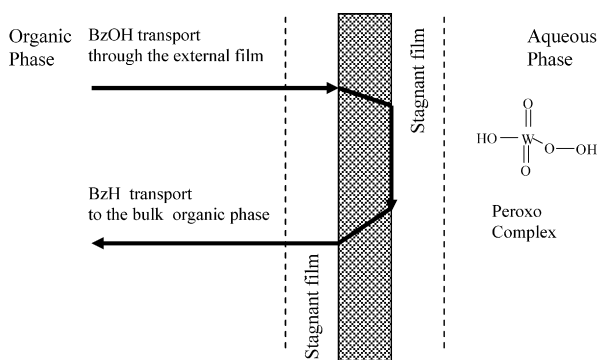
Table 1
Characteristics of the PVDF membranes used as membrane contactors

Membrane code	δ (μm)	r_p (μm)	ε	τ
M1	67	0.2	0.72	18.3
M2	50	0.07	0.65	43.6
M3	30	0.9	0.55	179

(DMA, reagent grade), acetone used as solvents, were purchased from Fluka; water, used for the coagulation bath, was double distilled.

3.2. Apparatus

Experimental tests were carried out in a simple reactor made with a two compartment cell to separate the organic and the aqueous phases (Fig. 1). The system was in a flat sheet configuration with a membrane surface area of 4.91×10^{-4} m^2.

The phases were stirred by magnetic stirrers and thermostated by a water bath at the different reaction temperatures tested (333 K, 343 K, 353 K).

Three different PVDF membranes, M1–M3, prepared by phase inversion induced by nonsolvent were used in the experiments according to different procedures reported in Ref. [21].

The polymer was dissolved at 25 °C (M1) and at 60 °C (M2) in the solvent DMA at 10 wt% and 12 wt%, respectively. The solutions were magnetically stirred for at least 1 day to guarantee complete dissolution of the polymer. The solutions were cast uniformly onto a glass substrate by means of a hand-casting knife (BRAIVE Instruments) with a knife gap set at 250 μm and then immediately immersed in a coagulation bath of water.

A different procedure was used for the preparation of M3.

The polymer (10 wt%) was dissolved at 25 °C in DMA (24 wt%) and acetone (64 wt%). The solution was magnetically stirred for 1 day to guarantee complete dissolution of the polymer.

The solution was casted onto a glass substrate by means of a hand-casting knife (BRAIVE Instruments) with a knife gap set at 250 μm and exposed to air for 3 h. Then, the cast film was immersed in a coagulation bath of water.

After complete coagulation, the membranes (M1–M3) were transferred into a pure water bath, which was refreshed frequently, for at least 24 h to remove the traces of solvent. The membranes were stored in a deionised water bath until tested for water permeability. For SEM, permporometry, contact angle, thickness measurements, the membrane samples were dried at 60 °C under vacuum.
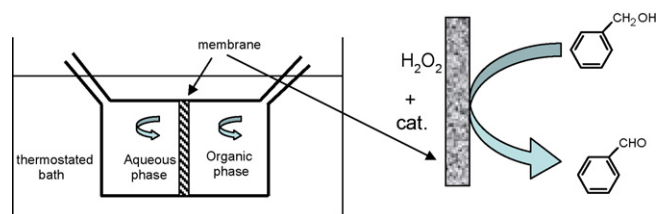

Scheme 2. Steps involved in the BzOH oxidation using a membrane contactor unit.

Fig. 1. Schematization of the used membrane reactor.

In Table 1, some important characteristics as thickness (δ), pore radius (r_p), overall porosity (ε), tortuosity (τ) of these membranes have been reported.

The membrane thickness was determined by a digital micrometer (Carl Mahr D 7300 Esslingen a.N.) and by SEM observation of the freeze-fractured cross-sections.

The overall porosity, ε, of the membranes was calculated according to Eq. (3):

$$\varepsilon = 100\% \times (1 - \text{density}_{\text{membrane}}/\text{density}_{\text{PVDF}}) \qquad (3)$$

in which the density of the membrane was determined gravimetrically by weighing a sample of known area and thickness, known density$_{\text{PVDF}}$ = 1.78.

Membrane pore dimensions (r_p) were determined by means of a capillary flow porometer CFP 1500 AEXL (Porous materials Inc. PMI, Ithaca, New York, USA).

The membrane tortuosity (τ) was calculated using Eq. (4):

$$R_m = \frac{\Delta P_{\text{tm}}}{J_w \eta_w} = \frac{32\tau\delta}{\varepsilon r_p^2} \qquad (4)$$

where ΔP_{tm} is the transmembrane pressure, R_m the hydraulic membrane resistance, η_w the water viscosity, J_w the water flux through the membrane [24].

The water flux measurements were carried out using an ultrafiltration setup, Separem Type UFSCP, consisting of five parallel filtration cells, each one offering an effective filtration area of 19.2 cm^2. ΔP_{tm} was varied from 1 bar to 4 bar and the temperature was fixed at 25 °C.

The morphology of the dried membranes (at 60 °C overnight) was examined using scanning electron microscopy (SEM), Cambridge, Stereoscan 360, at 20 kV. For cross-section analysis the membrane samples were freeze fractured in liquid nitrogen. All samples were sputter-coated with gold before analysis.

Contact angles of water droplets on the membrane surfaces were measured by sessile drop method using CAM 200 contact angle meter (KSV Instruments Ltd., Helsinki, Finland).

3.3. Oxidation reaction

In a typical experiment, the membrane was located between the cell compartments with the top surface from aqueous phase side. Two hundred millimolar of BzOH in one of the two cell compartment and in the other one, 15 mL of water, 4 mmol of catalyst and 199 mmol of H$_2$O$_2$ were loaded.

Obtained results are reported as selectivity to BzH, BzOH conversion to BzH, H$_2$O$_2$ conversion to BzH at a reaction time of 4 h.

3.4. Analysis

The analysis of the organic phase was carried by GLC using a 6890 network GC system of Agilent on a HP-5 (30 m × 0.320 mm × 0.25 μm) column.

The aqueous phase was analyzed for H$_2$O$_2$ by iodimetric titration using potassium iodide and sodium thiosulphate.

4. Results and discussion

The BzOH oxidation to BzH happens by the following reaction:

$$C_6H_5CH_2OH + H_2O_2 \xrightarrow{\text{cat}} C_6H_5CHO + 2H_2O$$
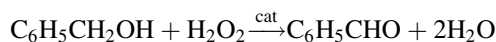
The reaction progress was investigated for different reaction temperatures, mode of addition of hydrogen peroxide, catalysts and types of membranes.

4.1. Effect of temperature on the progress of the reaction

Effect of reaction temperature on the progress of oxidation of BzOH was studied in the temperature range (333–353 K). The experimental results are reported in Figs. 2 and 3. It is observed in these experiments that BzOH conversion to BzH increased as temperature was raised, without a substantial loss of reaction selectivity (>97%).

In fact, conversion of BzOH to BzH from 17.4% at 333 K increased up to 74.3% operating at 353 K. The same trend was observed for hydrogen peroxide conversion: from 17.5% to 74.4%. Specifically, the strong effect on the production of BzH operating at different temperatures was clearly visible from the start of the reaction (Fig. 3). The production of BzH proceeded for 120 min with a similar trend operating at 343 K and 333 K ($\approx$70 g/L of BzH) whilst at 353 K a higher concentration of product was achieved (258 g/L). The different production of BzH at 343 K and 333 K became evident from 130 min to 240 min.

Chaudhary and Sawant [25] observed the same strong influence of the temperature on the progress of the BzOH oxidation made in a conventional reactor with the catalyst in the H$_2$O$_2$ aqueous phase. They classified this reaction as very slow reaction, kinetically controlled for which reaction temperature influences the progress of the reaction significantly.
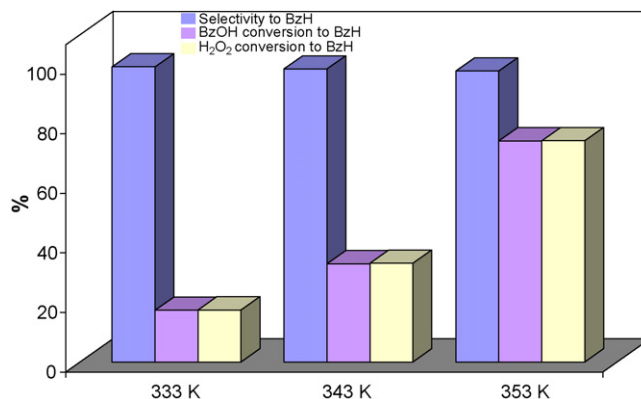

Fig. 2. Selectivity, BzOH and H$_2$O$_2$ conversion to BzH at different reaction temperatures (membrane M1; catalyst (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O; H$_2$O$_2$ added by pump mode in 1 h; reaction time 4 h). Selectivity to BzH = [mmol BzH/(mmol BzH + mmol BzA)] × 100. BzOH conversion to BzH = (mmol BzH/mmol BzOH initial) × 100. H$_2$O$_2$ conversion to BzH = (mmol BzH/mmol H$_2$O$_2$ initial) × 100.
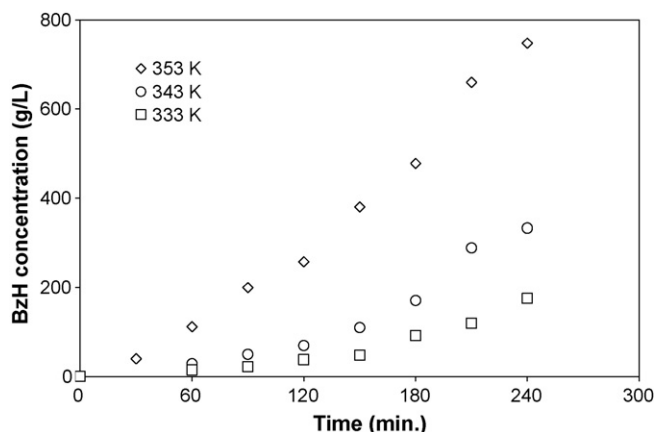
Fig. 3. BzH concentration in the organic phase vs. time at different reaction temperatures (membrane M1; catalyst $(NH_4)_6Mo_7O_{24}\cdot4H_2O$; H_2O_2 added by pump mode in 1 h).

4.2. Effect of hydrogen peroxide addition mode

The addition of hydrogen peroxide mode was another important parameter investigated. In particular a constant amount of hydrogen peroxide of 199 mol was added, testing two different ways: (i) one-step mode, with all H_2O_2 added at the start of the experimental run; (ii) pump mode, by adding the H_2O_2 slowly with a flow rate of 22.5 mL/h.

The experimental results are reported in Figs. 4 and 5.

The reaction with hydrogen peroxide added in one step proceeded for 90 min with a similar trend compared to the addition mode of the oxidant by pump (Fig. 4). Then, an evident difference of BzH conversion during the time was observed operating in the two ways: at 120 min, the BzH concentration was 25.8 g/L after 2 h in the first mode whilst 38 g/L for the second one; at 210 min the difference of BzH concentration in organic phase between the two addition modes is more of two times. The selectivity to BzH observed in the two cases is different, also is high: 96.0% for the first mode (one step), 99.2% for the second one (Fig. 5).
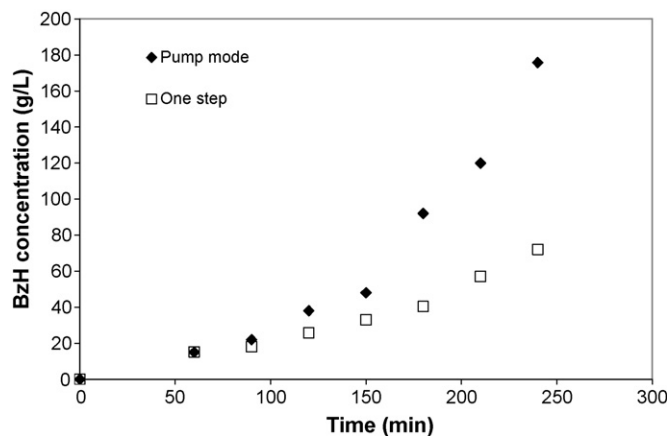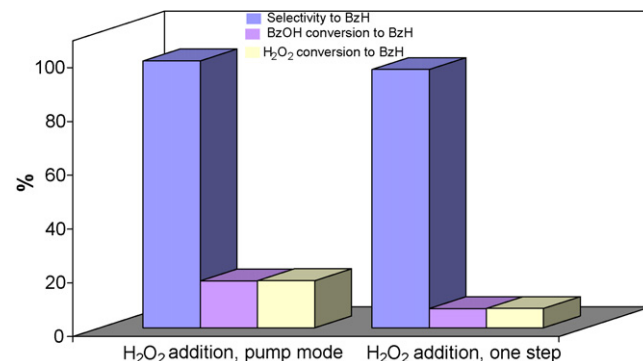

Fig. 5. Selectivity, BzOH and H_2O_2 conversion by changing the hydrogen peroxide addition mode (membrane M1; catalyst $(NH_4)_6Mo_7O_{24}\cdot4H_2O$; $T = 333$ K; reaction time 4 h).

H_2O_2 in the reaction mixture is consumed for oxidation of BzOH to BzH, which may be over oxidized to BzA; lost due to decomposition and unreacted in the reaction mixture. H_2O_2 consumed for the formation of product BzH and of by-product (BzA) was calculated; unreacted H_2O_2 was determined iodometrically and then H_2O_2 decomposed was calculated by difference.

In Fig. 6, the ratio of H_2O_2 consumed for oxidation of BzOH to H_2O_2 self decomposed as a function of reaction time is reported.

The plots of Fig. 6 indicated that H_2O_2 is more effectively consumed for the oxidation of BzOH when added in 1 h by means of the pump compared to the addition in one step.

4.3. Effect of the membrane characteristics

It is well known that the membrane porosity and pore sizes are two of the most important characteristics of all types of membranes. In a catalytic process, the membrane porosity and pore dimensions affect not only the permeation flux associated with the conversion and process capacity, but also the membrane catalytic efficiency and selectivity. In this study, in order to understand the effects of these membrane
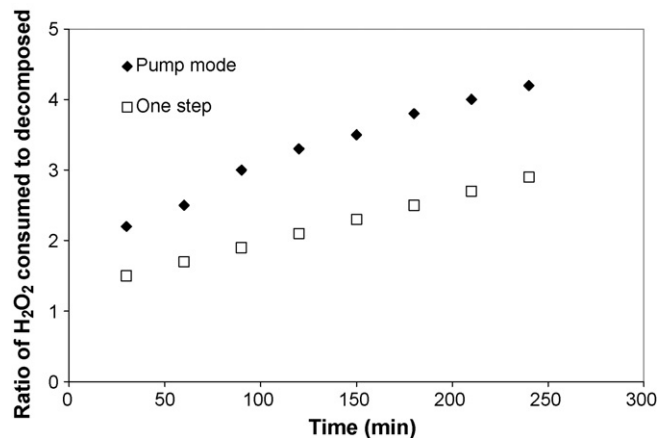

Fig. 4. BzH concentration in the organic phase vs. time by changing the hydrogen peroxide addition mode (membrane M1; catalyst $(NH_4)_6Mo_7O_{24}\cdot4H_2O$; $T = 333$ K).

Fig. 6. Ratio of H_2O_2 consumed for oxidation to H_2O_2 self-decomposed vs. time by changing the hydrogen peroxide addition mode (membrane M1; catalyst $(NH_4)_6Mo_7O_{24}\cdot4H_2O$; $T = 333$ K).

characteristics on the catalytic performance, three different asymmetric membranes (M1–M3) with different thicknesses, pore size and porosity (Table 1), but all based on PVDF were utilized. In Fig. 7, the SEM analysis of the membrane cross-sections and of the two surfaces (top and bottom) for the three membranes M1–M3 is shown.

M1 and M2 have a similar morphology characterized by the presence of macrovoids across the membrane cross-section on a thin skin layer. The structure of these two membranes is porous sponge in the bottom part, opposite to thin skin layer side. M3 is symmetric with a porous nodular structure. All the membranes surfaces are characterized by the presence of pores: the difference concerns their sizes as shown in Fig. 7 and Table 1.

Analyzing the selective side of the three membranes (top layer, Fig. 7(2)), M1 has pores of size of 0.2 μm, M2 has the smallest pores (0.07 μm). Due to the different preparation conditions which includes the presence of a volatile solvent added to that hydroscopic [21], membrane M3 has the biggest pores of 0.9 μm.

In Table 2, the contact angle to water for the two membrane sides of M1–M3 have been reported.

Table 2
Contact angle values to water (α) of M1–M3 for the two membrane layers (top and bottom)

Membrane	α (°)	
	Top layer	Bottom layer
M1	92 ± 2	123 ± 2
M2	80 ± 3	110 ± 3
M3	120 ± 2	122 ± 3

M3 has almost the same hydrophobic character for the two sides (top and bottom), with α value of $\approx 120°$. However, the top and bottom layers of M1 and M2 membranes have different properties: for both the membranes, the top surface is more hydrophilic (92° and 80° for M1 and M2, respectively) than the bottom layer (>110°, for both).

These different characteristics of hydrophobicity depended on the preparation conditions that are diverse for membranes M1, M2 compared to M3 as reported in literature [27].

During the reaction tests, the membranes were located in the membrane reactor with the top surface from the aqueous phase side. The results obtained are shown in Figs. 8 and 9.
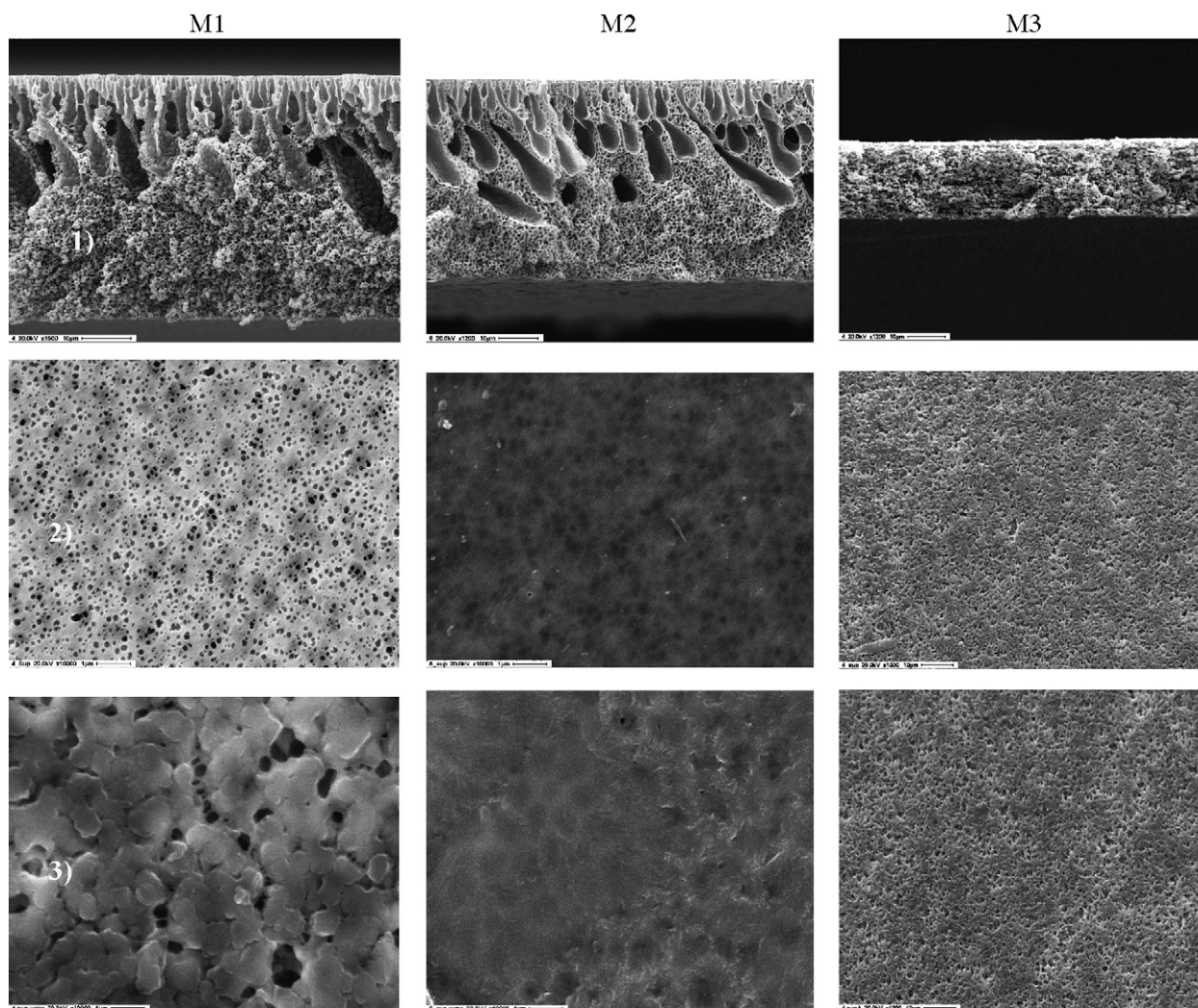

Fig. 7. SEM images of PVDF membranes tested in this work: cross-section (1), top layer (2) and bottom layer (3).
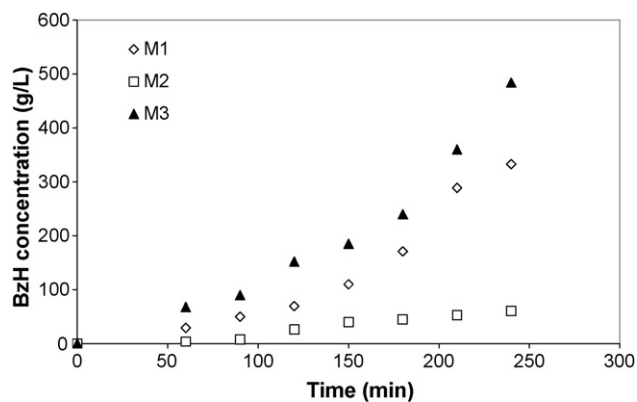
Fig. 8. BzH concentration in the organic phase vs. time testing three different membranes as membrane contactors, M1–M3 (catalyst $(NH_4)_6Mo_7O_{24}\cdot4H_2O$; H_2O_2 added by pump mode; $T = 343$ K).

The results reported in Fig. 8 show that the type of membrane used at the interface between the two reaction phases effected the formation of BzH. In particular, very good system performance was observed by using membrane M3. The membrane M2 showed the worst results: the formation of BzH reached a plateau after 150 min. At 240 min a concentration of 60.6 g/L was observed, very low value compared to the other ones obtained with M3 and M1, respectively of 484 g/L and 333 g/L.

It is noteworthy that no loss of selectivity using all the three membranes was observed (Fig. 9).

The reaction proceeded in three steps:

(1) BzOH permeation across the membrane from the bottom surface. The selective layer (top layer) was at the interface membrane-aqueous phase, being the bottom part of the membrane completely porous.
(2) Interfacial (membrane-aqueous phase) oxidation reaction.
(3) BzH (insoluble in the aqueous phase) permeation across the membrane to the organic phase.

The step 1 plays a crucial role to effect the performance of the conversion and for this reason we observed a difference
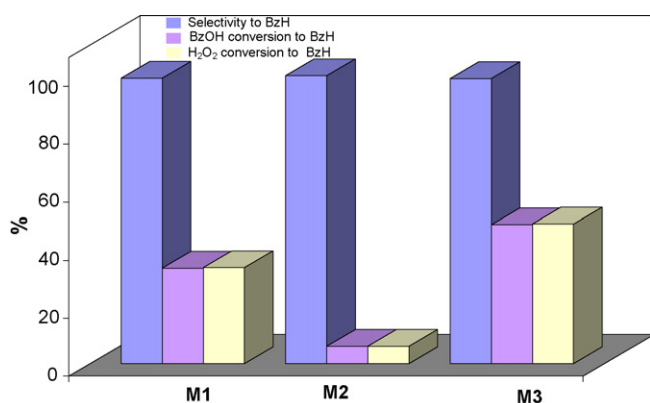

Fig. 9. Selectivity, BzOH and H_2O_2 conversion testing three different membranes as membrane contactors, M1–M3 (catalyst $(NH_4)_6Mo_7O_{24}\cdot4H_2O$; H_2O_2 added by pump mode; $T = 343$ K; reaction time 4 h).

Table 3
Some characteristics of the membranes base of Eq. (1)

Membrane	Θ	$\varepsilon/\tau \times 10^{-2}$
M1	0.980	3.93
M2	0.945	1.49
M3	0.995	0.307

using different membrane as contactors. On the basis of Eqs. (1) and (2), the diffusivity through a porous medium (D_{eff}) is in general effected by pore size of the porous structure (r_p), porosity (ε), tortuosity of the pore structure (τ). In particular, D_{eff} increases with the value of Θ (Eq. (2)) and it is inversely proportional to τ.

In Table 3, the ratio ε/τ and the factor Θ for the three membranes have been reported. For the calculation of Θ, the r_s of the molecules involved in the reaction is of ≈ 1 nm [26].

The factor Θ is almost the same for the three membranes, whilst a difference is observed for the values of ε/τ ratio. For membrane M3 the ratio ε/τ is the lowest, and on the basis of Eq. (1) the diffusivity across this membrane is lower compared to the ones of M1 and M2. However, the correlation low diffusivity and then low transport with the high conversion of BzOH observed using M3 is not direct. In fact, if the porosity (ε), tortuosity (τ), pore size (r_p) of the membranes are the only characteristics to explain the different reactivity observed with M1–M3, it is difficult to understand the difference of performance between M1 and M2.

Another important factor must be taken in account to rationalize the different reactivity observed changing the membrane, i.e. the hydrophilicity/hydrophobicity properties of the membranes.

Decreasing the water contact angle (α) of membrane top layer in the order M3 > M1 > M2, water wettability increased: water filled membrane pores and hindered the transport from organic to aqueous phase, increasing the membrane resistance (R_m) to mass transport from organic phase to aqueous phase. In fact, M3 with a top layer of 120° has lower water wettability and in this case low R_m; however, at the opposite, using M2 characterized by a water contact angle of 80°, aqueous phase wets the membrane and higher R_m to organic transport from organic to aqueous interface occurred. Therefore, the observed trend for the performance in terms of conversion (Fig. 9) i.e. M3 > M1 > M2, reflected the different hydrophobicity properties of the membrane top layers in contact with the aqueous phase (Table 2).

4.4. Effect of different catalysts

Another factor studied in this work was the type of catalyst. Oxodiperoxo and peroxo complexes of Mo(VI) and W(VI) with H_2O_2 are well known oxidants used for oxidation of organic compounds [28]. Hence, the effect of $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ on the conversion of BzOH was compared with that of $Na_2WO_4\cdot2H_2O$ using membrane M1 and operating at 343 K adding (by pump) of hydrogen peroxide. In Figs. 10 and 11 the results of catalytic tests have been reported.
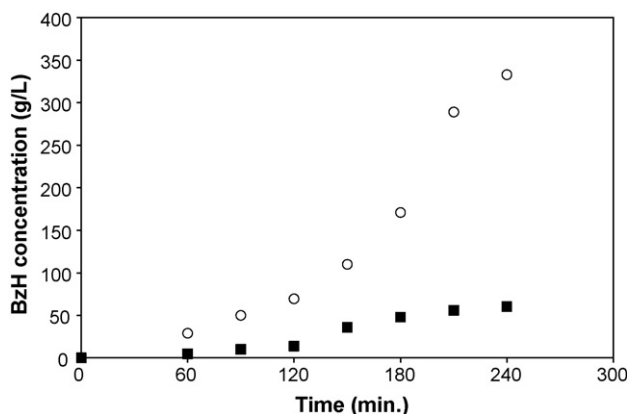
Fig. 10. BzH concentration in the organic phase vs. time using (○) $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and (■) $Na_2WO_4\cdot2H_2O$ as catalysts (membrane M1; H_2O_2 added by pump mode; $T = 343$ K).
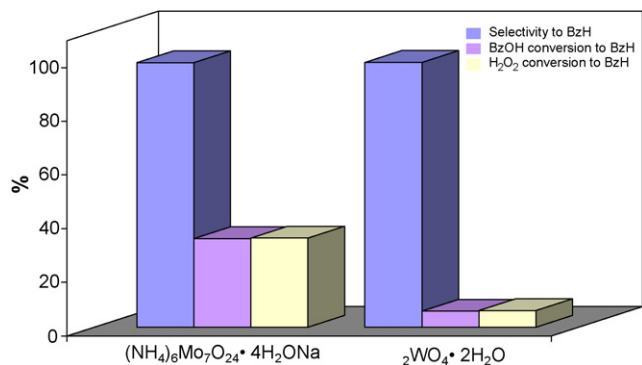
Fig. 11. Selectivity, BzOH and H_2O_2 conversion using $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ and $Na_2WO_4\cdot2H_2O$ as catalysts (membrane M1; H_2O_2 added by pump mode; $T = 343$ K; reaction time 4 h).

Ammonium molybdate gave higher formation of BzH during the time (333 g/L, at 240 min) compared to that with sodium tungstate (60.6 g/L).

Bortolini et al. [14] observed that the oxidation of alcohols catalyzed by $Na_2WO_4\cdot2H_2O$ in the presence of a phase transfer catalyst gave high conversions when excesses ranging from 2-fold to 6-fold of hydrogen peroxide are used. In particular, with BzOH larger excesses of H_2O_2 over the substrate lead the formation of BzA [14].

In this work, no over oxidation to BzA occurs with both the catalysts as the selectivity observed indicated (Fig. 11). Influence of the pH of catalyst solution is under investigation and further research with other secondary alcohols is in progress.

5. Conclusions

In this work, it was possible to demonstrate that the principle of using a catalytic membrane as interphase contactor in a biphase reaction in neat conditions is feasible.

BzOH can be oxidized selectively to benzaldehyde with hydrogen peroxide as oxidizing agent and ammonium molybdate and sodium tungstate as catalysts. Between these two catalysts used, ammonium molybdate was found to be the best catalyst for oxidation of BzOH. Using this catalyst, the reported results show that hydrogen peroxide pumped for 1 h in the aqueous phase, M3 as membrane contactor, a reaction temperature of 353 K gave the best system performance in terms of selectivity to BzH (98%) and BzOH conversion (74%).

It has been found that this system with a membrane contactor across the two reaction phases does not only work to produce BzH, but also essentially separates the product from the aqueous phase. Compared with the conventional reactor, the membrane plays a role similar to a phase transfer catalyst without need of organic solvents.

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